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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : A01N 57/12, A61K 25/26 — A1

(11) International Publication Number: WO 97/09882

(43) International Publication Date: 20 March 1997 (20.03.97)

(21) International Application Number: PCT/US96/13717

(22) International Filing Date: 30 August 1996 (30.08.96)

(30) Priority Data:
08/527,982 14 September 1995 (14.09.95) US

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(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: PHOSPHOROAMIDOTHIOATE COATED SAND AND METHOD

(57) Abstract

A chemically stable, insecticidally active composition comprising sand having coated thereon a binder and 0.1 to 25.0 weight percent, based on the total weight of the composition of at least one insecticidally active phosphoroamidothioate, wherein the binder is a compatible non-aqueous, non-volatile liquid. A method for improving the chemical stability of a coated, insecticidally active phosphoroamidothioate composition comprises coating at least one insecticidally active phosphoroamidothioate compound on sand.

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PHOSPHOROAMIDOTHIOATE COATED SAND AND METHOD

FIELD OF THE INVENTION

The present invention is directed to the achievement of chemically stable, insecticidally active phosphoroamidothioate compositions. In particular, the present invention is directed to insecticidally active phosphoroamidothioate compositions based on the extremely good stability afforded by the use of sand. Thus, the present invention is directed to chemically stable, insecticidally active compositions in which at least one insecticidally active phosphoroamidothioate compound has been coated on sand, and the present invention is also directed to a method for improving the chemical stability of a coated, insecticidally active composition by coating at least one insecticidally active phosphoroamidothioate compound on sand.

BACKGROUND OF THE INVENTION

Insecticidally active compositions in various forms have been developed for diverse applications. The method of preparation of the insecticidally active composition is largely determined by the physical and chemical nature of the insecticide and the intended use and method of application of the insecticide to the area to be treated.

Certain phosphoroamidothioates and phosphoroamidodithioates ("phosphoroamidothioates") are known in the art as having excellent insecticidal activity against a variety of insects and in a variety of environments. A particularly important commercial insecticide within these classes of compounds is the

insecticide acephate (generic name) or Orthene® (tradename), which can be systemically taken up by a plant so that insects which feed and/or live on the plant are killed, in addition to those insects which directly ingest or are contacted by the insecticide. Acephate and related compounds are described in U.S. Patent Nos. 3,716,600, 3,845,172 and 3,914,417, which disclose that in addition to their insecticidal properties, the compounds possess very low mammalian toxicity. Orthene® is commercially produced as a technical grade chemical of about 97 to 99.5% purity.

One method of formulating technical grade phosphoroamidothioates for commercial use is to mix the technical grade powder with an anti-caking agent, such as fumed silica, and a wetting agent. The wetting agent is utilized to wet the insecticide and the anti-caking agent, and the anti-caking agent is used to prevent agglomeration of the insecticide in its container. This formulation of insecticide can be applied to crops as a spray solution or as a dust.

The use of phosphoroamidothioates as powders allows for relatively high concentrations of insecticide to be applied to a treatment area, but the powder application suffers from various disadvantages. First, the finely divided particles of active spray may be carried by air currents into areas where harmful effects may occur. In addition, it is difficult to apply sprays or dusts to the soil surface or to lower areas of plants when dense foliage must be penetrated. Also, the powder has a bad odor. Additionally, in its powder form, it becomes airborne easily, and it is perceived as a health hazard. Finally, powdered phosphoroamidothioates suffer from

chemical stability problems due to hydrolytic and catalytically-driven degradation, which shortens the shelf life of the powdered insecticide.

While the use of acephate in granular form (e.g., pellets) would overcome some of the inherent difficulties involved in using sprays or dusts, granular formulations suffer from various problems.

One problem in granular compositions is the presence of dry additives and processing aids such as diluents, lubricants, flowability agents, surfactants, etc., which have been determined to aggravate the chemical stability problems of insecticidally active phosphoroamidothioates. In turn, the lack of chemical stability for granular insecticidally active phosphoroamidothioates interferes with the commercial feasibility of such formulations.

Furthermore, methods such as pan granulation and extrusion (pelletizing), which have been used to make granules, have adverse effects on insecticidally active phosphoroamidothioates like Orthene®.

Pan granulation employs water, and the granules which are initially produced contain a significant amount of water. As a result, a dryer is used to remove the water from the granules. However, Orthene® degrades in water and is heat-sensitive, so the use of pan granulation is disadvantageous for producing Orthene® formulations.

In regard to pelletization processes, U.S. Patents 5,075,058 and 5,100,667 describe processes for pelletizing formulations containing insecticides such as phosphoroamidothioates. In particular, U.S. Patent 5,075,058 discloses a process for forming pellets by extruding a mixture of Orthene®, a second active

ingredient, and optional components such as a limited amount of ammonium sulfate, and U.S. Patent 5,100,667 exemplifies a process for forming pellets of Orthene® alone or in combination with a surfactant and ammonium sulfate using a pellet mill. However, pellet mills or extruders used to form pellets from mixtures containing Orthene® can generate heat. As noted above, Orthene® is heat-sensitive, so pelletizing is disadvantageous for producing Orthene® formulations, particularly low strength formulations.

To satisfy the need in the art for a low cost, highly effective, chemically stable, insecticidally active phosphoroamidothioate granular formulation, one of the present inventors developed an insecticidally active composition comprising particles prepared by the compaction of an admixture comprising ammonium sulfate and at least one insecticidally active phosphoroamidothioate. This composition and methods for its manufacture and use are described in U.S. Patents 5,298,501, 5,352,674, and 5,369,100. As set forth in these patents, it was found that the use of ammonium sulfate in particular leads to a compacted composition which provides a high degree of chemical stability.

While the aforementioned composition provides excellent chemical stability, it was found that low strength formulations as the technology teaches could not be made hard enough by compaction to be useful from a practical perspective.

Thus, there is a need in the art for chemically stable, low strength, insecticidally active phosphoroamidothioate formulations which are useful from a practical standpoint.

SUMMARY OF THE INVENTION

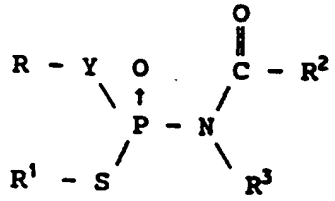
In view of the above problems in the art, an object of the present invention is to provide chemically stable, low strength, insecticidally active phosphoroamidothioate formulations which are useful from a practical standpoint. In this regard, it is noted that an object of the present invention is to provide a chemically stable, low strength, insecticidally active formulation which is based in particular on at least one insecticidally active phosphoroamidothioate rather than on any other insecticidally active compounds. A characteristic feature of the present invention is the coating of at least one insecticidally active phosphoroamidothioate (rather than some other insecticidally active compound) on sand (rather than on another core material).

In an attempt to satisfy the above and other objectives, the present inventors turned to a coating process in which Orthene® was coated on various cores.

In one test, Orthene® was coated on an ammonium sulfate core. Such a composition was expected to be satisfactory, since ammonium sulfate had been used successfully in the compaction process. Surprisingly, though, formulations in which Orthene® was coated on an ammonium sulfate core provided poor chemical stability.

Numerous other embodiments were tested as well, in which Orthene® was coated on various cores. After conducting extensive research and development, the present inventors discovered that low strength formulations in which Orthene® is coated on sand in particular provide excellent chemical stability, and thus the above and other objects were obtained.

Accordingly, in one of its aspects, the present invention is directed to an insecticidally active composition comprising sand having coated thereon components comprising a binder and at least one insecticidally active compound of the formula:



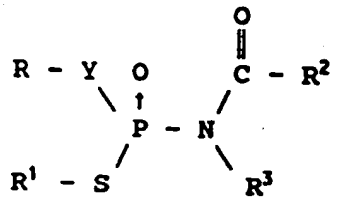
wherein R and R^1 individually are an alkyl, alkenyl or alkynyl group containing up to 6 carbon atoms, R^2 is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms or an alkynyl group containing 3 to 18 carbon atoms, R^3 is hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Y is oxygen or sulfur,

wherein the binder is a nonaqueous, nonvolatile liquid which does not have an adverse effect on chemical stability of the composition, and

wherein the at least one insecticidally active compound is present in an amount of from 0.1 to 25.0 weight percent, based on the total weight of the composition.

In another of its aspects, the present invention is directed to a method for improving chemical stability of a coated, insecticidally active phosphoroamidothioate composition, comprising coating sand with components

comprising a binder and at least one insecticidally active compound of the formula:



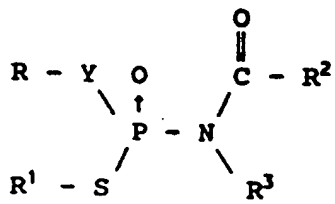
wherein R and R^1 individually are an alkyl, alkenyl or alkynyl group containing up to 6 carbon atoms, R^2 is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms or an alkynyl group containing 3 to 18 carbon atoms, R^3 is hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Y is oxygen or sulfur,

wherein the binder is a nonaqueous, nonvolatile liquid which does not have an adverse effect on chemical stability of the composition, and

wherein the at least one insecticidally active compound is present in an amount of from 0.1 to 25.0 weight percent, based on the total weight of the composition.

DETAILED DESCRIPTION OF THE INVENTION

The term "phosphoroamidothioate" refers to a compound or a mixture of compounds of the formula:



wherein R and R^1 individually are an alkyl, alkenyl or alkynyl group containing up to 6 carbon atoms, R^2 is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms or an alkynyl group containing 3 to 18 carbon atoms, R^3 is hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Y is oxygen or sulfur.

Particularly preferred compounds are those in which R and R^1 are independently a methyl, ethyl, allyl or alkenyl group; R^2 is H or an alkyl group; R^3 is hydrogen; and Y is oxygen. The most preferred compound is that in which R, R^1, and R^2 are methyl groups, R^3 is hydrogen and Y is oxygen. Compounds of the above formula may be prepared as described in U.S. Patent Nos. 3,176,600, 3,845,172 and 3,914,417, which are incorporated herein by reference in their entirety. Likewise, acephate (R, R^1, R^2 are CH_3; R^3 is hydrogen and Y is oxygen) is commercially available from Chevron Chemical Company, San Ramon, California (e.g., Orthene® 90S (90% acephate), Orthene® 80S (80% acephate) and Orthene® 75S (75% acephate)).

One or a mixture of the above compounds forms the insecticidally active component in the formulation of this invention. The amount of insecticidally active component in the invention formulation can be from about 0.1 to about 25.0 weight percent, based on the total weight of the composition. Preferably, the insecticidally active component is present in an amount of from about 0.1 to about 10.0 weight percent, and more preferably, the insecticidally active component is present in an amount of from about 0.5 to about 5.0

weight percent. In a particularly preferred embodiment, the insecticidally active component is present in an amount of about 2.5 weight percent.

An important feature of the present invention is the discovery that for coated formulations which contain an insecticidally active phosphoroamidothioate, the insecticidally active phosphoroamidothioate should be coated on sand, rather than on some other core material, in order to achieve good chemical stability. If the sand is replaced with a seemingly similar material (e.g., granules of ammonium sulfate, which is usually considered to be an inert, non-porous material), the chemical stability of the formulation is adversely affected.

This discovery is important, because it is desirable to have low strength, insecticidally active phosphoroamidothioate formulations which are chemically stable and which are usable from a practical perspective.

Thus, for the core of the present invention, sand is used. Sand is a mineralogically defined form of silicon dioxide and specifically is a gritty or particulate form of the chemical. In general, sand particles can be quite angular and rough and can have sharp edges, like a diamond, or they can be rather smooth, almost spherical, like ball bearings. The particles that are relatively smooth are referred to as subangular. It is preferred for the sand to be subangular in the present invention so that the coating can be built up and so that there are no sharp edges to peel off the coating.

The sand particle size can be selected from a wide range of sizes. Typical sizes include:

U.S. Mesh	Diameter
8/16	2360 micron/0.0937" to 1190 micron/0.0469"
16/30	1190 micron/0.0469" to 590 micron/0.0232"
20/40	840 micron/0.0331" to 420 micron/0.0165"
30/50	590 micron/0.0232" to 297 micron/0.0117"

The insecticidally active phosphoroamidothioate adheres to the sand core via a binder. That is, the sand core is coated with a binder, and the insecticidally active phosphoroamidothioate adheres to the binder-coated sand core. It should be noted that the process can be initiated by mixing the insecticidally active phosphoroamidothioate and the sand and then adding the binder.

The binder can be any nonaqueous, nonvolatile liquid which does not adversely affect the chemical stability of the insecticidally active composition. A key feature of the binder is that it is a material which is nonvolatile, thereby allowing a continuous film coating to be formed without the use of heat or any chemical reaction. Preferably, the insecticidally active component is not soluble in the binder.

Many conventionally-used solvents can act as binders in the present invention as long as they meet the aforementioned requirements. For example, suitable binders include refined soybean oil, refined cottonseed oil, refined corn oil, peanut oil, diethylene glycol, isopropylbiphenyl (e.g., Sure Sol-330, manufactured by Koch Chemical Company, Corpus Christi, Texas), alkylphenyl polyether alcohol (e.g., Enviromark 3, manufactured by Formulogics, Inc., Trenton, New Jersey), propylene glycol, d-limonene (d-p-mentha-1,8 diene), mineral oils (e.g., Klearol and Blandol, manufactured by

Witco Chemical Corp., Greenwich, Connecticut), paraffinic spray oil (e.g., Orchex 692, manufactured by Exxon Chemical Company, Houston, Texas), isoparaffinic solvent (e.g., Isopar L, manufactured by Exxon Chemical Company), alkyl acetates (e.g., Exxate 100, manufactured by Exxon Chemical Company), and alkyl naphthalenic solvent (e.g., Aromatic 200, manufactured by Exxon Chemical Company). N-methylpyrrolidone is an example of a binder which is not suitable for the present invention, because it has an adverse effect on the chemical stability of the composition, as can be seen from the experimentation set forth subsequently. Other binders which should not be used are water-soluble binders and heat-setting binders, because of the deleterious impact of water and/or heat on the chemical stability.

The amount of binder which is used can range from about 0.1 to about 15.0 weight percent, based on the total weight of the composition. Preferably, the binder is present in an amount of from about 0.1 to about 10.0 weight percent, and more preferably, the binder is present in an amount of from about 0.5 to about 5.0 weight percent. In a particularly preferred embodiment, the binder is present in an amount of from about 0.5 to about 2.0 weight percent.

In the event that the granules are too damp, a drying agent can be added to the formulation to obtain dry, free-flowing granules. Suitable drying agents can be selected from classes of finely divided carriers which do not adversely affect the chemical stability of the insecticidally active phosphoroamidothioate. Suitable drying agents include, by way of example, hydrated silica and other highly absorptive silicas, such as fumed

silica, although it should be noted that drying agents other than silica-based drying agents can also be used.

The drying agent can be present in an amount of up to about 6 weight percent, preferably up to about 5 weight percent, based on the total weight of the composition.

Other additives can be included in the composition as desired in suitable amounts. In particular, other additives can be reodorants, bittering agents, colorants, and other finely divided carriers. For example, rhodamine dye can be included in the composition. It is important that additive or additives used do not adversely affect the chemical stability of the insecticidally active phosphoroamidothioate.

In some embodiments of the present invention, other pesticides (either solid or liquid) can be added in suitable amounts. A nonvolatile liquid pesticide may even be used as the binder, if chemically compatible. It is important that additional pesticide or pesticides used do not adversely affect the chemical stability of the insecticidally active phosphoroamidothioate.

In other embodiments of the present invention, no active ingredients are present other than the insecticidally active phosphoroamidothioate active ingredient.

The composition of the present invention can be made as follows. First, sand and a binder are placed in a mixer (e.g., a Continental mixer), and the mixer is operated so that the sand is uniformly coated with the binder. Then, the insecticidally active phosphoroamidothioate is added to the mixer, and the mixer is operated so that the insecticidally active

phosphoroamidothioate uniformly adheres to the binder-coated sand. If the granules are too damp, a drying agent can be added to provide a dry, free-flowing granular product.

Alternatively, the process can be initiated by mixing the insecticidally active phosphoroamidothioate and the sand and then adding the binder.

An insecticidally active composition made in accordance with the present invention has very good chemical stability. Very good chemical stability can be considered as meaning that the amount of the insecticidally active phosphoroamidothioates in the formulation does not diminish by more than about 10% when stored under accelerated storage conditions of 28 days at 50-55°C as compared to the amount of the phosphoroamidothioates in the formulation at the time of preparation. Under these accelerated conditions, insecticidally active phosphoroamidothioate particles which do not experience more than about a 10% decrease in the amount of the phosphoroamidothioate evidence the fact that such particles will possess very good long term storage stability under ambient conditions.

It should be noted that the 10% degradation maximum is a minimally acceptable target for defining shelf life and that much less degradation is highly preferable.

Once formulated, the particles are useful in a method for controlling insects by application of the particles onto the insects' habitat. In general, the particles can be applied onto the habitat in an amount sufficient to provide acceptable control of the insects. In a preferred embodiment, the particles are applied at a rate of at least about 0.5 lb (0.227 kg) acephate per

acre and more preferably at a rate of from about 0.5 lb (0.227 kg) to about 2.0 lbs (0.909 kg) acephate per acre (0.004 square kilometer). Obviously, the amount of particles to be applied per acre (0.004 square kilometer) will depend upon the concentration of acephate in the particles. Thus, for example, particles containing 5% acephate will need to be applied at 10 lbs (2.27 kg) per acre (0.004 square kilometer) to achieve a dosage of 0.5 lb (0.227 kg) acephate per acre (0.004 square kilometer).

The following examples illustrate specific embodiments of the invention but should not be construed as limiting the scope of the claims in any way. All parts, percents, ratios and the like are by weight unless otherwise indicated.

EXAMPLES

Example 1

The purpose of this example is to investigate the chemical stability of insecticidally active phosphoroamidothioate embodiments having a sand core, particularly with the use of various binders.

Granules of sand were added to a jar, and then a liquid binder as set forth below in Tables 1-3 was added. The jar was tumbled/shaken to uniformly coat/treat the granules. De-lumped Orthene® Tech (which contains 97-99% acephate) was then added, and the jar was tumbled/shaken to adhere the Orthene® to the binder-coated granules. In addition, Hi-Sil 532ED or Hi-Sil 233 (hydrated silica) was added to achieve a dry, free-flowing granular. The amount of each component which was used is shown in Tables 1-3 below. The samples were placed into glass jars which were sealed for aging.

The samples were analyzed to provide an initial active ingredient concentration (which was obtained by assaying a sample following one month aging in a freezer at -20°F (samples do not degrade measurably at this temperature)) and active ingredient concentrations after various time periods and at temperatures to determine the amount of active ingredient degradation and thereby evaluate the chemical stability of the compositions. The results are shown below in Tables 1-3.

Table 1

	A	B	C	D	E	F	G	H	I	J
Orthene Tech	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Hi-Sil 532ED	0.7	0.7	0.7	0.7	0.9	0.7	0.7	0.7	0.7	0.7
Cottonseed Oil	1.2	1.2	X	X	X	X	X	X	X	X
Soybean Oil	X	X	1.2	1.2	1.6	X	X	X	X	X
Corn Oil	X	X	X	X	X	1.2	1.2	X	X	X
Peanut Oil	X	X	X	X	X	X	X	1.2	1.2	X
Aromatic 200	X	X	X	X	X	X	X	X	X	1.2
Sand	95.6	95.6	95.6	95.6	95.0	95.6	95.6	95.6	95.6	95.6
Assay, % Acephate Initial	2.4	2.4	2.5	2.4	2.5	2.5	2.5	2.5	2.5	2.6
One Month 50°C	2.4	2.5	2.4	2.4	2.5	2.3	2.5	2.4	2.5	2.4
Two Month 50°C	2.4	2.5	2.5	2.6	2.2	2.4	2.5	2.4	2.4	3.0
Three Month Ambient	2.5	2.4	2.3	2.5	-	2.3	2.5	2.3	2.4	2.2
50°C	2.4	2.4	2.5	2.3	-	2.3	2.5	2.3	2.0	2.4

Table 2

	K	L	M	N	O
Orthene Tech	2.5	2.5	2.5	2.5	5.0
Hi-Sil 532ED	0.7	0.7	0.7	0.7	1.8
Enviromark 3	1.2	X	X	X	2.3
Klearol	X	1.2	X	X	X
Isopar L	X	X	1.2	X	X
Exxate 100	X	X	X	1.2	X
Sand	95.6	95.6	95.6	95.6	90.9
Assay, % Acephate Initial	2.5	2.3	2.4	2.7	4.5
One Month 50°C	2.3	2.3	3.0	2.7	4.7
Two Month 50°C	2.5	2.3	2.2	2.7	4.7
Three Month Ambient 50°C	2.5 2.2	2.3 2.1	2.2 2.0	2.1 2.1	- -

Table 3

	P	Q	R	S
Orthene Tech	2.5%	2.5	2.5	2.5
Sand, 20/40 mesh	93.0	95.0	90.9	93.2
Cottonseed Oil	1.8	X	X	X
Aromatic 200	X	1.0	X	X
N-methylpyrrolidone	X	X	1.5	X
Enviromark 3	X	X	X	1.3
Hi-Sil 233	2.7	1.5	5.1	3.0
Assay, % Acephate Initial	2.4	2.8	2.5	2.0
One Month 50°C	2.3	2.3	1.6	2.0
Two Month 37°C 50°C	2.6 2.1	3.0 2.4	2.0 0.6	2.2 2.2
Three Month Ambient 50°C	2.3 1.7	2.5 1.9	2.8 0.1	2.1 1.2

As can be seen from the results set forth above, virtually all of the tested invention embodiments provided very good chemical stability (it should be noted that the dashes which appear for two of the embodiments in the tables mean that no assays were conducted). As described above, very good chemical stability is considered to be obtained where the amount of the insecticidally active phosphoroamidothioates in the

formulation does not diminish by more than about 10% when stored under accelerated storage conditions of 28 days at 50-55°C as compared to the amount of the phosphoroamidothioates in the formulation at the time of preparation. Under these accelerated conditions, insecticidally active phosphoroamidothioate particles which do not experience more than about a 10% decrease in the amount of the phosphoroamidothioate evidence the fact that such particles will possess very good long term storage stability under ambient conditions. The embodiment which had the poorest performance was the embodiment in which N-methylpyrrolidone was used as the binder. As noted in the detailed description above, N-methylpyrrolidone is a binder which has an adverse effect on chemical stability of insecticidally active phosphoroamidothioates compositions and thus would not be included within the scope of the present invention. With respect to the invention embodiments, essentially all of the tested embodiments within the scope of the present invention had very good chemical stability.

Example 2

The purpose of this example is to demonstrate the poor chemical stability which was obtained when ammonium sulfate was used as the core in the coated, insecticidally active phosporoamidothioate composition instead of using sand. As noted above, this result was surprising in view of the very good chemical stability which was obtained with the use of ammonium sulfate in compacted particles.

Granules of ammonium sulfate were added to a jar. Then, a liquid binder as set forth below in Table 4 was

added, and the jar was tumbled/shaken to uniformly coat the granules. De-lumped Orthene® Tech was then added, and the jar was tumbled/shaken to adhere the Orthene® to the binder-coated granules. Where the granules were too damp, Hi-Sil 233 was added to achieve a dry, free-flowing granular. The amount of each component which was used is shown below in Table 4. The samples were placed into glass jars which were sealed for aging.

The samples were analyzed to provide an initial active ingredient concentration (which was obtained by assaying a sample following one month aging in a freezer at -20°F) and active ingredient concentrations after various time periods and temperatures to determine the amount of active ingredient degradation and thereby evaluate the chemical stability of the compositions. The results are shown below in Table 4.

Table 4

	T	U	V	W	X	Y	Z	AA	BB	CC	DD
Orthene Tech	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Ammonium Sulfate, granular	96.0	95.8	94.5	95.8	95.8	95.8	95.8	95.7	95.3	95.7	95.8
Hi-Sil 233	0.5	X	1.0	X	X	X	X	0.1	0.5	X	X
Cottonseed Oil	1.0	1.7	X	X	X	X	X	X	X	X	X
Water	X	X	2.0	X	X	X	X	X	X	X	X
Propylene glycol	X	X	X	1.7	X	X	X	X	X	X	X
Diethylene Glycol	X	X	X	X	1.7	X	X	X	X	X	X
ABP-103	X	X	X	X	X	1.7	X	X	X	X	X
Orchex 692	X	X	X	X	X	X	1.7	X	X	X	X
Enviromark 3	X	X	X	X	X	X	X	1.7	X	X	X
N-methylpyrrolidone	X	X	X	X	X	X	X	X	1.7	X	X
Aromatic 200	X	X	X	X	X	X	X	X	X	1.8	X
d-limonene	X	X	X	X	X	X	X	X	X	X	1.7
Assay, % Acephate Initial	2.5	2.2	2.3	2.1	2.2	2.3	2.6	2.6	2.2	2.6	2.4
One Month 50°C	1.9	1.1	0	0.2	0.2	1.6	2.0	1.4	0.6	1.6	1.5
Two Month 37°C 50°C	2.1 1.7	1.7 0.7	0.2 0	0.8 0	1.3 0	2.2 0.3	1.9 1.2	1.8 0.6	1.3 0.1	1.8 0.8	1.6 0.5
Three Month Ambient 50°C	2.3 0.7	2.2 0	2.8 0	1.2 0	1.6 0	2.2 0	2.1 0.1	2.3 0.1	1.1 0	2.3 0	2.1 0.1

As can be seen from the results set forth above, particularly in regard to the evaluations at the 50°C temperature condition for accelerated aging (which would provide some indication of the long term chemical stability under ambient conditions), the samples suffered from significant degradation. Thus, while ammonium sulfate provides good results when used in a compaction method involving insecticidally active phosphoroamidothioates, it provides surprisingly poor results when used as the core in a coating method involving insecticidally active phosphoroamidothioates.

Example 3

The purpose of this example is to further demonstrate the significance of employing sand, rather than another conventionally-used material, as the core in the coated, insecticidally active composition. It is noted that in this example, the sand-based embodiments had a higher insecticidally active phosphoroamidothioate amount than in Example 1, thereby demonstrating the unexpected superiority of present invention over the recited range of insecticidally active phosphoroamidothioate content.

Granules of either Biodac (a cellulosic-based granule) or sand were added to a jar, and then the liquid binder (in this case, refined soybean oil) was added. The jar was tumbled/shaken to uniformly coat/treat the granules. Orthene® 90S (which contains 90% acephate, with the remainder being inerts such as silica and surfactant) was then added, and the jar was tumbled/shaken to uniformly adhere the Orthene® to the binder-coated granules. Where the granules were too

damp, Hi-Sil 233 was added to achieve a dry, free-flowing granular. Rhodamine dye was added in a similar manner to the addition of the Orthene® 90S. The amount of each component which was used is shown in Table 5 below. The samples were placed into glass jars which were sealed for aging. With respect to the sand-based samples, Sample FF was bottled as produced and had lumps consisting of agglomerates of the sand, binder and Orthene® 90S present rather than individual particles, while Sample GG was screened prior to bottling and thus was expected to be more uniform.

The samples were analyzed to provide an initial active ingredient concentration (which was obtained by assaying a sample following one month aging in a freezer at -20°F) and active ingredient concentrations after one month of aging at temperatures of 18°C, 33°C and 44°C to determine the amount of active ingredient degradation and thereby evaluate the chemical stability of the compositions. The results are shown below in Table 5.

Table 5

	EE	FF	GG
Orthene 90S	10.0	24.4	21.8
Sand, 40/70 mesh	X	66.5	66.2
Biodac 18/30 mesh	75.0	X	X
Refined soybean oil	15.0	7.8	10.3
Hi-Sil 233	X	1.29	1.69
Rhodamine B	X	0.01	0.01
Initial Assay	9.3	12.8	18.3
One month - 18°C 33°C 44°C	8.3 7.6 5.8	18.9 16.3 17.9	16.0 15.8 16.0

As can be seen from the results set forth above, the sample based on a Biodac core suffered from significant degradation, while the samples based on a sand core did not experience significant degradation (the increase in active ingredient concentration in Sample FF might be attributed to the non-uniformity of the sample due to lack of screening). Thus, the sand-based insecticidally active phosphoroamidothioate compositions provided very good chemical stability as compared with the Biodac-based insecticidally active phosphoroamidothioate composition.

Example 4

The purpose of this example is to further demonstrate that insecticidally active phosphoroamidothioate compositions containing the conventionally-used material Biodac as the core do not have good chemical stability.

Granules of Biodac were added to a jar. Then, soybean oil was added as the binder, and the jar was tumbled/shaken to uniformly coat the granules. De-lumped Orthene® Tech was then added, and the jar was tumbled/shaken to adhere the Orthene® to the binder-coated granules. The amount of each component which was used is shown below in Table 6. The samples were placed into glass jars which were sealed for aging.

The samples were analyzed to provide a zero time active ingredient concentration and active ingredient concentrations after various time periods at 50°C to determine the amount of active ingredient degradation and thereby evaluate the chemical stability of the compositions. The results are shown below in Table 6.

Table 6

	HH	II
Orthene Tech	2.5	5.0
Soybean Oil	12.7	14.7
Biodac Granules	84.8	80.3
Assay, % Acephate Initial	1.8	3.8
One Month 50°C	0	0
Two Month 50°C	0	0

As can be seen from the results set forth above, the samples suffered from significant degradation. Thus, it can be seen that insecticidally active phosphoroamidothioate embodiments having the conventionally-used material Biodac as their core do not have good chemical stability.

Thus, the data set forth above show that unexpectedly superior chemical stability can be obtained when an insecticidally active phosphoroamidothioate is coated on sand rather than on another material, particularly where the binder which is used to adhere the insecticidally active phosphoroamidothioate to the sand is a binder which itself does not adversely affect the chemical stability of the insecticidally active phosphoroamidothioate.

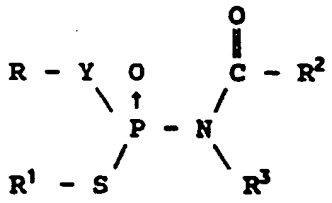
Because the insecticidally active composition of the present invention is chemically stable, use of this composition in methods for controlling insects will

provide very good results as compared with compositions used previously, because a smaller amount of insecticidally active phosphoroamidothioate will degrade over time.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. A chemically stable, insecticidally active composition comprising sand having coated thereon components comprising a binder and at least one insecticidally active compound of the formula:



wherein R and R^1 individually are an alkyl, alkenyl or alkynyl group containing up to 6 carbon atoms, R^2 is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms or an alkynyl group containing 3 to 18 carbon atoms, R^3 is hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Y is oxygen or sulfur,

wherein the binder is a nonaqueous, nonvolatile liquid which does not have an adverse effect on chemical stability of the composition, and

wherein the at least one insecticidally active compound is present in an amount of from 0.1 to 25.0 weight percent, based on the total weight of the composition.

2. A chemically stable, insecticidally active composition as claimed in claim 1, wherein said at least one insecticidally active compound is present in an

amount of from 0.1 to 10.0 weight percent, based on the total weight of the composition.

3. A chemically stable, insecticidally active composition as claimed in claim 1, wherein said at least one insecticidally active compound is present in an amount of from 0.5 to 5.0 weight percent, based on the total weight of the composition.

4. A chemically stable, insecticidally active composition as claimed in claim 2, wherein the sand is subangular sand.

5. A chemically stable, insecticidally active composition as claimed in claim 3, wherein the sand is subangular sand.

6. A chemically stable, insecticidally active composition as claimed in claim 2, wherein the binder is present in an amount of from 0.1 to 10.0 weight percent, based on the total weight of the composition.

7. A chemically stable, insecticidally active composition as claimed in claim 3, wherein the binder is present in an amount of from 0.5 to 5.0 weight percent, based on the total weight of the composition.

8. A chemically stable, insecticidally active composition as claimed in claim 2, wherein the binder is selected from the group consisting of refined soybean oil, refined cottonseed oil, refined corn oil, peanut oil, diethylene glycol, isopropylbiphenyl, alkylphenyl

polyether alcohol, propylene glycol, d-limonene, mineral oils, paraffinic spray oil, isoparaffinic solvent, alkyl acetates, and alkyl naphthalenic solvent.

9. A chemically stable, insecticidally active composition as claimed in claim 3, wherein the binder is selected from the group consisting of refined soybean oil, refined cottonseed oil, refined corn oil, peanut oil, diethylene glycol, isopropylbiphenyl, alkylphenyl polyether alcohol, propylene glycol, d-limonene, mineral oils, paraffinic spray oil, isoparaffinic solvent, alkyl acetates, and alkyl naphthalenic solvent.

10. A chemically stable, insecticidally active composition as claimed in claim 2, wherein the components further comprise a drying agent present in an amount of up to 5 weight percent, based on the total weight of the composition.

11. A chemically stable, insecticidally active composition as claimed in claim 3, wherein the components further comprise a drying agent present in an amount of up to 5 weight percent, based on the total weight of the composition.

12. A chemically stable, insecticidally active composition as claimed in claim 2, wherein the components consist essentially of the binder and the at least one insecticidally active compound.

13. A chemically stable, insecticidally active composition as claimed in claim 3, wherein the components

consist essentially of the binder and the at least one insecticidally active compound.

14. A chemically stable, insecticidally active composition as claimed in claim 10, wherein the components consist essentially of the binder, the at least one insecticidally active compound, and the drying agent.

15. A chemically stable, insecticidally active composition as claimed in claim 11, wherein the components consist essentially of the binder, the at least one insecticidally active compound, and the drying agent.

16. A chemically stable, insecticidally active composition as claimed in claim 2, wherein no active ingredient is present other than the at least one insecticidally active compound.

17. A chemically stable, insecticidally active composition as claimed in claim 3, wherein no active ingredient is present other than the at least one insecticidally active compound.

18. A chemically stable, insecticidally active composition as claimed in claim 12, wherein no active ingredient is present other than the at least one insecticidally active compound.

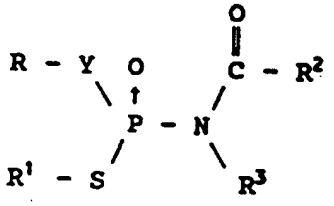
19. A chemically stable, insecticidally active composition as claimed in claim 13, wherein no active

ingredient is present other than the at least one insecticidally active compound.

20. A chemically stable, insecticidally active composition as claimed in claim 14, wherein no active ingredient is present other than the at least one insecticidally active compound.

21. A chemically stable, insecticidally active composition as claimed in claim 15, wherein no active ingredient is present other than the at least one insecticidally active compound.

22. A method for improving chemical stability of a coated, insecticidally active phosphoroamidothioate composition, comprising coating sand with components comprising a binder and at least one insecticidally active compound of the formula:



wherein R and R^1 individually are an alkyl, alkenyl or alkynyl group containing up to 6 carbon atoms, R^2 is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containing 2 to 18 carbon atoms or an alkynyl group containing 3 to 18 carbon atoms, R^3 is

hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Y is oxygen or sulfur,

wherein the binder is a nonaqueous, nonvolatile liquid which does not have an adverse effect on chemical stability of the composition, and

wherein the at least one insecticidally active compound is present in an amount of from 0.1 to 25.0 weight percent, based on the total weight of the composition.

23. A method for improving chemical stability of a coated, insecticidally active phosphoroamidothioate composition as claimed in claim 22, wherein said at least one insecticidally active compound is present in an amount of from 0.1 to 10.0 weight percent, based on the total weight of the composition.

24. A method for improving chemical stability of a coated, insecticidally active phosphoroamidothioate composition as claimed in claim 22, wherein said at least one insecticidally active compound is present in an amount of from 0.5 to 5.0 weight percent, based on the total weight of the composition.

25. A method for improving chemical stability of a coated, insecticidally active phosphoroamidothioate composition as claimed in claim 23, wherein the components further comprise a drying agent present in an amount of up to 5 weight percent, based on the total weight of the composition.

26. A method for improving chemical stability of a coated, insecticidally active phosphoroamidothioate composition as claimed in claim 24, wherein the components further comprise a drying agent present in an amount of up to 5 weight percent, based on the total weight of the composition.

27. A method for improving chemical stability of a coated, insecticidally active phosphoroamidothioate composition as claimed in claim 23, wherein the components consist essentially of the binder and the at least one insecticidally active compound.

28. A method for improving chemical stability of a coated, insecticidally active phosphoroamidothioate composition as claimed in claim 24, wherein the components consist essentially of the binder and the at least one insecticidally active compound.

29. A method for improving chemical stability of a coated, insecticidally active phosphoroamidothioate composition as claimed in claim 25, wherein the components consist essentially of the binder, the at least one insecticidally active compound, and the drying agent.

30. A method for improving chemical stability of a coated, insecticidally active phosphoroamidothioate composition as claimed in claim 26, wherein the components consist essentially of the binder, the at least one insecticidally active compound, and the drying agent.

31. A method for improving chemical stability of a coated, insecticidally active phosphoroamidothioate composition as claimed in claim 27, wherein no active ingredient is present other than the at least one insecticidally active compound.

32. A method for improving chemical stability of a coated, insecticidally active phosphoroamidothioate composition as claimed in claim 28, wherein no active ingredient is present other than the at least one insecticidally active compound.

33. A method for improving chemical stability of a coated, insecticidally active phosphoroamidothioate composition as claimed in claim 29, wherein no active ingredient is present other than the at least one insecticidally active compound.

34. A method for improving chemical stability of a coated, insecticidally active phosphoroamidothioate composition as claimed in claim 30, wherein no active ingredient is present other than the at least one insecticidally active compound.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/13717

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : A01N 57/12; A61K 25/26
US CL :424/421; 427/212; 558/178

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/421; 427/212; 558/178

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,716,600 (MAGEE) 13 February 1973, see column 18.	1-34
Y	US, A, 3,845,172 (MAGEE) 29 October 1974, see column 15, line 1 to column 16, line 58.	1-34
Y	US, A, 4,855,309 (KOCH ET AL.) 08 August 1989, see column 10, lines 32-39.	1-34
Y	US, A, 4,954,529 (KOCH ET AL.) 04 September 1990, see column 7, lines 31-37.	1-34
Y	US, A, 5,169,644 (MOLLS ET AL.) 08 December 1992, see entire document.	1-34
Y	US, A, 5,326,573 (ANTFANG ET AL.) 05 July 1994, see entire document.	1-34

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 OCTOBER 1996	07 NOV 1996
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer ROBERT H. HARRISON Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet)(July 1992)*